Neutral and cationic Fe(II) beta-diketiminate complexes

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Supplementary Material for :

Neutral and Cationic Fe(II) β-Diketiminate Complexes

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*IR data (KBr, nujol mull) for compounds **1**–**4***

1: $\widetilde{\nu}$ = 3057, 3013, 1594 (m), 1524 (s), 1484 (m), 1437, 1318, 1261 (s), 1203, 1176, 1099, 1056, 1029, 1021, 992, 934 (m), 859 (w), 794, 758, 743, 695 (m), 579, 521 (w), 438 (m) cm^{-1}.

2: $\widetilde{\nu}$ = 2909 (s), 1526 (s), 1317 (s), 1289 (m), 1252 (m), 1239 (s), 1175 (m), 1099 (m), 1023 (w), 934 (m), 917 (m), 904 (m), 850 (m), 818 (m), 794 (m), 755 (s), 743 (w), 726 (m), 498 (w), 468 (w), 435 (w) cm^{-1}.

3: $\widetilde{\nu}$ = 3104 (w), 3058, 3026 (m), 1925, 1862 (m), 1800 (w), 1591 (m), 1514 (s), 1454, 1314 (s), 1277 (m), 1254 (s), 1224, 1208 (m), 1173 (s), 1154, 1099, 1057, 1039, 1025, 1004 (m), 966 (s), 934 (m), 900, 883 (w), 845, 790(m), 751, 729, 699 (s), 628, 574 (w), 556, 528 (m), 464 (w), 426 (m) cm^{-1}.

4: $\widetilde{\nu}$ = 1640(m), 1514(s), 1314, 1276, 1260, 1176, 1082(m), 1058, 1027(w), 979(s), 935(m), 893, 829, 781, 759, 534(w) cm^{-1}.

*^{1}H NMR data in THF-d_8 for **1*** (500 MHz, RT) *and **2*** (300 MHz, RT)

1: δ ($\Delta\nu_{½}$, integral, assignment) = 36.2 (80 Hz, 2H, *m*-H_{Ph}), 12.0 (55 Hz, 4H, *m*-H_{Ar}), 1.2 (98, 12H, *i*Pr-CH_3), –19.2 (623, 2H, *o*-H_{Ph}), –25.4 (234, 12H, *i*Pr-CH_3), –27.9 (546, 1H, α-H), –41.2 (1212, 4H, *i*Pr-CH), –43.6 (58.2, 2H, *p*-H_{Ar}), –50.1 (65.5, 1H, *p*-H_{Ph}), –55.7 (176, 6H, γ-Me) ppm.

2: δ ($\Delta\nu_{½}$, integral, assignment) = 51.5 (587 Hz, 1H, α-CH), 41.5 (300 Hz, 9H, $Si(CH_3)_3$), 17.0 (266 Hz, 6H, γ-CH_3), –0.0 (27 Hz, 4H, *m*-H), –7.2 (87 Hz, 12H, *i*Pr-CH_3), –55.9 (56 Hz, 2H, *p*-H), –66.1 (382 Hz, 12H, *i*Pr-CH_3), –88.1 (1512 Hz, 4H, *i*Pr-CH) ppm.

*Generation of **1** from [(^{Me}BDK)$FeCl_2$]*[1] *and $PhCH_2MgBr$*

A 1.43 M solution of $PhCH_2MgBr$ in Et_2O (0.38 mL, 0.55 mm) was added to a stirred solution of [(^{Me}BDK)$FeCl_2$] (150 mg, 0.28 mmol) in Et_2O (20 mL). The solution changed colour from purple to red/brown *via* yellow. The solution was stirred at room temperature for 30 min. Et_2O was removed under reduced pressure and the residue was stirred in pentane (20 mL) and evaporated to dryness to remove residual Et_2O (2x). The residue was extracted with pentane (20 mL, 2x) to give a bright orange extract, leaving a grey salt. Pentane was removed *in vacuo* giving a dark red oil. The iron complex was not purified by crystallisation but the oil was dissolved directly in C_6D_6 for identification of the products by ^{1}H NMR spectroscopy and GC-MS analysis.

*Preparation of **2** from [(^{Me}BDK)$FeCl_2$]*[1] *and $LiCH_2SiMe_3$*

A solution of $LiCH_2SiMe_3$ (100 mg, 1.07 mmol) in pentane (5 mL) was added to a stirred suspension of [(^{Me}BDK)$FeCl_2$] (290 mg, 0.53 mmol) in pentane (10 mL). The reaction mixture was stirred at room temperature for 30 min. while the purple suspension turned yellow and a white salt precipitated. The finely divided LiCl was allowed to settle for 18 hrs at –25 ºC and was filtered off. The residue was extracted once more with pentane (10 mL). The volume was concentrated to *ca.* 50% and crystallisation at –30 ºC afforded **2** as yellow needles. Yield: 52 mg (19%).

[1] A. Panda; M. Stender; R. J. Wright; M M. Olmstead; P. Klavins; P. P. Power, Inorg. Chem. 41 (2002) 3909.